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SYNTHESIS OF A NEW MODIFICATION OF ALUMINUM OXIDE, GAHNITE, AND ZINCITE IN DETONATION

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Results of studying the products of explosion of aluminum and octogen charges enclosed by a brass shell under conditions of complete burning out in air are described. Gahnite $ZnAl_2O_4$, a new (metastable) modification of aluminum oxide, and small quantities of zinc oxide were identified in the condensed explosion products. The x-ray pattern of the aluminum oxide was indexed in a face-centered cubic lattice with the parameters $a = 7.854(1) \text{ \AA}$, $V = 484.4(2) \text{ \AA}^3$. The possible Fedorov groups are $Fm\bar{3}m$, $F432$, and $F43m$.

We previously reported the synthesis of new metastable crystalline modifications of silicon, silicon carbide, and aluminum oxide in detonation of metallized explosive mixtures. One of the reasons for retention of metastable crystalline modifications under the conditions of the experiment is rapid cooling of the explosion products in conservation installations.

Calculation of the equilibrium constants of the water gas reaction for the products of explosion of hexogen and octogen, which serve as the basis for explosive mixtures, shows that the composition of the gas phase is “frozen” at a temperature of 1400–1600 K. However, when certain metals (B, Al, Mg, Ti, Zr, etc.) are present in the initial explosive mixture, the final composition of the gaseous products of explosion can set at a lower temperature, due to additional reactions with the participation of the metals.

The present paper discusses results of a physicochemical study of the products of explosion of a mixture of aluminum (grade PP-1, particle size below 10 μm) and octogen. Mixtures with an aluminum content of 30, 40, and 50 wt.% were prepared by simple mechanical mixing of the components until a homogenous mixture was obtained.

The experiments were conducted in a thick-walled steel vessel with an internal volume of 16 liters (a Bichel bomb). A charge 20 mm in diameter weighing 10 g was placed at the center of the bomb. The bulk density of the explosive material in the charge was 0.8–0.9 g/cm^3 . The charge was enclosed by a thick-walled cylindrical brass shell (wall thickness 7.5 mm, height 58 mm, shell weight 307 g). The bomb with a massive steel lid was reliably sealed using pressure

bolts and lead gaskets. An excessive air pressure (0.1 MPa) was developed inside the bomb before the experiment. The detonation was initiated by exploding a lead azide charge weighing 0.1 g (Fig. 1).

The small weight of the charge and the corresponding excessive air pressure should ensure complete burning of the products formed in the explosion.

Table 1 shows data of a thermodynamic calculation of the composition of the explosion products after gas-dynamic equilibrium is established inside the reaction vessel, but before they started cooling (an adiabatic explosion). Components whose content in the explosion products is below 10^{-3} mole/kg are not specified in Table 1. According to the calculation, the only condensed product generated by the explosion of aluminum and octogen mixtures under the conditions selected should be aluminum oxide. The maximum temperature inside the reaction vessel can reach 2700–3200 K.

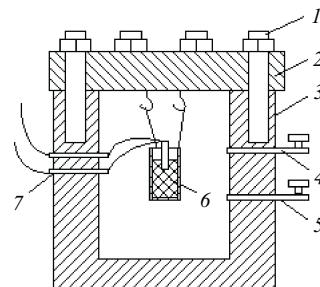


Fig. 1. Bichel bomb: 1) pressure bolts; 2) bomb lid; 3) bomb casing; 4) valve for pressure gauge and evacuation; 5) valve for gas removal; 6) explosive charge in a shell and initiator; 7) explosive line.

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TABLE 1

Mixture composition in reaction vessel, g-atom/kg	Equilibrium composition of explosion products, mole/kg												Temper- ature of explo- sion, ** K	
	N ₂	NO ₂	NO	H ₂ O _(gas)	H ₂	H	OH	CO ₂	CO	O ₂	O	Al ₂ O _{3(cond)}	ΣM _(gas) [*]	
C _{1.995} H _{3.991} N _{47.200} O _{15.474} Al _{2.347}	23.306	0.001	0.586	1.869	0.017	0.008	0.210	1.879	0.116	2.674	0.061	1.174	30.727	2664
C _{1.711} H _{3.423} N _{46.629} O _{14.905} Al _{3.128}	22.948	0.001	0.731	1.502	0.037	0.026	0.317	1.452	0.260	2.178	0.136	1.564	29.588	2899
C _{1.523} H _{3.046} N _{45.460} O _{14.325} Al _{4.177}	22.304	0.001	0.850	1.128	0.098	0.109	0.483	0.904	0.618	1.423	0.320	2.088	28.238	3221

* Amount of emerging gaseous products of the explosion.

** The pressure in the reaction vessel was 2.1 MPa.

TABLE 2

Composition of mixture in reaction vessel, mole/kg	Composition of explosion products, mole /kg						Energy release of explosion, kcal/kg	Residual pressure, MPa
	N ₂	CO ₂	O ₂	H ₂ O _(cond)	Al ₂ O _{3(cond)}	Al _(cond)		
0.499C ₄ H ₈ N ₈ O ₈ + 2.345Al + 5.740O ₂ + 21.610N ₂	23.82	1.94	3.05	1.94	1.14	0	28.81	3815.5
0.428C ₄ H ₈ N ₈ O ₈ + 3.126Al + 5.740O ₂ + 21.610N ₂	23.48	1.70	2.55	1.66	1.52	0	27.73	4337.0
0.381C ₄ H ₈ N ₈ O ₈ + 4.175Al + 5.640O ₂ + 21.220N ₂	22.93	1.51	1.95	1.48	1.97	0.11	26.39	4743.5

After cooling the reaction vessel to room temperature (20°C), the residual pressure was measured, and the volume of the gaseous products of the explosion was calculated. The composition of the gases was determined on an LKhM-72 chromatograph.

Data of the chromatographic analysis of the gases appearing in the explosion and results of a calculation of the condensed-phase composition based on the material and heat balance equation under the assumption of aluminum oxide formation, as follows from the thermodynamic calculation, are shown in Table 2. The investigation indicated that under the conditions of the experiment, aluminum in each case burns up almost completely. The energy release of the explosion of the 50% mixture of aluminum and octogen, provided that the explosion products burn up completely in air, is equal to 4743 kcal/kg, which is 4.5 times higher than the energy release of a trotyl explosion.

X-ray spectral and phase analyses established that the condensed-phase composition is more complex than the calculated phase composition.

The composition of the condensed explosion products was determined using a micro-x-ray-spectral method on a Link QX 2000 scanning microscope, which allows for element identification starting with sodium. The experimental results indicate that the condensed-phase particles have a homogeneous composition. In addition to aluminum, zinc and copper are present in them.

The x-ray phase analysis of the condensed products of the explosion was carried out on a STADI-P auto-diffractometer (germanium as the monochromator and CuK_{α1} radiation) and in an FR-552 monochromator focusing chamber (CuK_{α1} radiation, germanium as the internal standard). The

diffraction patterns were processed according to a software program developed by STOE. The x-ray patterns were measured on an IZA-2 comparator.

The expected α-Al₂O₃ lines were absent in all x-ray patterns of the condensed phases. Lines of gahnite ZnAl₂O₄ and a phase whose x-ray pattern is shown in Table 3 are most intense and sharpest. The contents of these phases in the explosion products considered are equal. Of the three copper lines with *hkl* = 111, 200, and 220 that could theoretically be registered on the x-ray pattern, only the most intense line, that is, 111, was noticeable. The other two lines coincided with lines of gahnite and the second phase. The x-ray patterns of the condensed phase that formed in the explosion of the mixtures with 30 and 40% aluminum content exhibited eight lines of a hexagonal modification of zinc oxide with *hkl* = 100, 002, 101, 102, 110, 103, 201, and 112. The interplanar distances of ZnO correlated with a hexagonal lattice with the parameters (Å) *a* = 3.241(2) and *c* = 5.201(4).

Gahnite is a normal spinel with an extensive region of homogeneity. The spinel ZnAl₂O₄ of stoichiometric composition has the lattice parameter *a* = 8.088 Å [1]. A higher value of this parameter (8.099 Å) is observed in a natural sample of talc shale, in which 20 zinc atoms are replaced by magnesium [2]. The crystal-chemical formula of this sample is (Zn_{0.79}Mg_{0.21})(Al_{1.90}Mg_{0.25}Fe_{0.075})O₄. Annealing at temperatures of 1000 and 1200°C did not cause a perceptible redistribution of the cations in the lattice.

When nonstoichiometric spinel ZnAl₂O₄ decomposes within the temperature interval 850 – 1200°C, the following compounds are identified: Zn₄Al₂₂O₃₇ (11Al₂O₃ · 4ZnO) with the hexagonal lattice (Å) *a* = 5.679 and *c* = 13.71 (PDF

TABLE 3

Intensity	Interplanar distance D_e , $Q = 10^4/D_e^2$ Å	hkl	$Q = 10^4/D_s^2$	ΔQ
100	4.5352	486.19	111	486.37
53	3.9281	648.09	200	648.49
40	2.7759	1297.75	220	1296.99
58	2.3687	1782.30	311	1783.36
53	2.2673	1945.28	222	1945.48
35	1.9653	2589.06	400	2593.98
28	1.8024	3078.21	331	3080.35
22	1.7570	3239.34	420	3242.47
22	1.6033	3890.19	422	3890.97
15	1.3083	5842.32	442	5836.45
				5.87

ICPDS 23-1491) and $Zn_6Al_{94}O_{144}$ ($94Al_2O_3 \cdot 6ZnO$) crystallizing in a monoclinic system with $a = 9.30$ Å, $b = 5.63$ Å, $c = 12.10$ Å, $\beta = 103^\circ 43'$ (PDF ICPDS 23-1490). In compositions with the ratio $Al_2O_3 : ZnO$ exceeding 99, a compound with the lattice parameters $a = 5.62$ Å, $b = 2.91$ Å, $c = 11.78$ Å, and $\beta = 104^\circ 09'$ (PDF ICPDS 22-1034), which coincide with the lattice parameters of $\theta-Al_2O_3$ (PDF ICPDS 35-121), was identified.

At a temperature over 1200°C, volatilization of zinc oxide is registered, and the lattice parameter decreases [3].

All lines of gahnite on the x-ray pattern of the condensed phase formed in the explosion of the mixture with 30% aluminum content were indexed with the lattice parameter $a = 8.097(2)$ Å, and in the case of the mixture with 40% aluminum content, the lines were indexed with the parameter $a = 8.093(3)$ Å. A smaller parameter (8.084(3) Å) was found in the lattice of gahnite identified in the condensed explosion products of the mixture with 50% aluminum content.

Ten lines of the second basic phase were indexed in a face-centered cubic lattice with $a = 7.854(1)$ Å, $V = 484.4(2)$ Å³ (Table 3). The indexing criteria are $M_{10} = 115$, $F_{10} = 45$; the possible Fedorov symmetry groups are $Fm3m$, $F432$, and $F43m$.

In [4], in studying the $Al_2O_3 - ZrO_2$ system it was possible to identify a high-temperature modification $\epsilon-Al_2O_3$ with the hexagonal lattice (Å) $a = 7.849$ and $c = 16.183$. The parameter a in $\epsilon-Al_2O_3$ does not differ significantly from the parameter a in the cubic phase discovered by us in the condensed products of the explosion of aluminum and octogen mixtures.

The condensed explosion products were annealed in air for 3 h at temperatures of 400, 600, and 800°C. The x-ray pattern of the sample annealed at a temperature of 400°C exhibits lines of $ZnAl_2O_4$ with a smaller lattice parameter 8.086(3) Å and the most intense lines of zinc oxide. The lines of the phase with the cubic face-centered lattice disappeared. However, some new lines of medium intensity appeared. They were indexed in a primitive rhombic lattice with $a = 5.731(7)$ Å, $b = 5.652(7)$ Å, $c = 5.464(5)$ Å, $V = 176.2(5)$ Å³.

After annealing at 600°C, the gahnite line with $hkl = 111$ became visible, and the intensity of the ZnO lines became much weaker. The x-ray pattern of the products annealed at 800°C exhibited mainly $ZnAl_2O_4$ lines with the lattice parameter 8.083(2) Å.

The cited results of the x-ray studies of the condensed products of explosion of aluminum and octogen mixtures and published data on the thermal stability of $ZnAl_2O_4$ and synthesis of $\epsilon-Al_2O_3$ [4] suggest that in our experiments, just as in [5], we were able to synthesize two coherently coupled phases (phases of coherent ingrowth) with a face-centered cubic lattice, namely, $ZnAl_2O_4$ and a metastable aluminum oxide that was previously unknown.

Aluminum ions in these phases exist inside an octahedral environment of oxygen ions. In the gahnite structure, aluminum ions are arranged in octahedral positions of cubic packing of oxygen ions. The aluminum oxide presumably has a structure that is similar to the cubic structure $C-M_2O_3$ observed in In_2O_3 , Tl_2O_3 , Mn_2O_3 , and sesquioxides of rare-earth elements. Aluminum ions are arranged like Ca^{2+} ions in fluorite, and oxygen atoms possibly occupy 3/4 of the positions of fluorine in such a way that not only the cubic symmetry but also the Bravais type of lattice is retained.

The large number of oxygen compounds of zinc identified in the products of explosion of aluminum and octogen mixtures indicates that the brass shell enclosing the charge is intensely destroyed in detonation, with subsequent selective burning up of the zinc. This became possible because the experiments were conducted under conditions of excess oxidant. In the normal practice of carrying out experiments in precision explosive calorimetry, secondary reactions of the explosion products with the shell material are excluded, since the explosion occurs in a vacuum and the charge is enclosed by a thick-walled inert shell [6].

A calculation based on concepts developed in [7] indicates that the amount of zinc needed for formation of gahnite (3–4 g) can be thrust into the reaction zone only during the mechanical destruction of the shell surface layer under the action of a strong shock wave. Simple heating of the shell in the detonation wave produces an amount of zinc that is an order of magnitude smaller (0.1 g).

The investigation performed points to the possibility of developing a method for detonation synthesis of oxide phases with complex compositions and complex crystalline lattices by using explosive devices with separate placement of the reacting components.

REFERENCES

1. R. F. Cooley and J. S. Reed, "Equilibrium cation distribution in $NiAl_2O_4$, $CuAl_2O_4$ and $ZnAl_2O_4$ spinels," *Am. Ceram. Soc.*, **55**(8), 395–398 (1972).
2. H. Saalfeld, "Structural data for gahnite, $ZnAl_2O_4$," *Zeit. Kristal.*, **120**(6), 476–478 (1964).

3. F. Colin and J. Thery, "Chemical properties of mixed oxides based on alumina: reduction of the spinels $MgAl_2O_4$ and $ZnAl_2O_4$," *Rev. Chim. Miner.*, **3**(1), 121 – 134 (1966).
4. G. Cevales, "Das Zustandsdiagramm Al_2O_3 – ZrO_2 und die Bestimmung einer neuen Hochtemperaturphase (ϵ - Al_2O_3)," *Ber. Dtsch. Keram. Ges.*, **45**(5), 216 – 219 (1968).
5. A. N. Tsvigunov, V. G. Khotin, S. E. Kuznetsov, etc., "A new modification of silicon obtained under an explosive action," *Steklo Keram.*, No. 9, 22 – 25 (1995).
6. R. McGayre, D. Ornellaas, and I. Akst, "Chemistry of detonation processes: diffusion phenomena in non-ideal explosive compounds," in: *Detonation and Explosive Materials* [Russian translation], Mir, Moscow (1981), pp. 160 – 169.
7. A. N. Afanasenkov, V. M. Bogomolov, and I. M. Voskoboinikov, "The calculation of parameters of the detonation wave of explosive mixtures with inert additives," *Fiz. Gorenija Vzryva*, No. 2, 182 – 186 (1970).